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(54) AGGLOMERATED METAL SHOT

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AGGLOMERATED METAL SHOT

This invention is concerned with the production of metal shot from fine metallic powders such as lead and iron. A process is provided for agglomerating the powder into balls of good sphericity, low porosity and acceptable strength, without the use of expensive dies or molds, or large shot towers. The resulting balls are held together by a cold-welding effect between particles or by an adhesive.

The invention provides strong spherical agglomerates of metal powder prepared in two-phase liquid systems, with the dispersed liquid phase preferentially wetting the powder being aqueous or an aqueous-base adhesive. The agglomerated powder becomes bound together by the adhesive or by a cold-welding effect on impact shaping. For bird shot, the adhesive may be water-sensitive causing the pellet to disintegrate slowly in a moist environment.

Previously such metal shot has been prepared by melting and casting, by powder metallurgy techniques, or by shot tower techniques where molten metal is sprayed into a cooling fluid and shaped by surface tension effects. It has been difficult to obtain good sphericity without a surface finishing or grinding step, and the equipment needed for large volume production is quite extensive.

An object of the present invention is to provide a process for uniting and shaping metal powder into pellets having good sphericity, strength and density. Another object is to provide such pellets of heavy metal powder united by an adhesive or by a cold-welding or -forging effect. A further object is to provide such pellets which will slowly disintegrate in a moist or aqueous environment.

It has recently been suggested that metal shot that would disintegrate under moist conditions would be useful to

prevent the ingestion and retention of spent shot by feeding water fowl and thus reduce the incidence of poisoning that is believed to occur when massive shot composed of toxic materials such as lead, is ingested. Should such a pellet be picked up it would disintegrate reasonably quickly in the bird's crop and pass through the digestive tract rapdily. For ballistic reasons the shot should be as dense as possible and have sufficient strength (in compression) to withstand the acceleration in the gun barrel, as well as the impact of hitting the target.

The process of the invention includes adding the metal powder and an aqueous liquid which wets the powder to an inert organic liquid and agitating to form agglomerates of powder plus aqueous liquid the agglomerates then being forced to undergo a continued impact and ricocheting action. This may suitably be accomplished by enclosing the mixture in an incompletely filled container having rounded inner surfaces. The container is then shaken at a frequency and in a pattern causing agglomerates of the powder and aqueous liquid to undergo an impact and ricocheting action against the container walls. This shaking is prolonged until the desired balls have been produced. This shaking action is more fully described in Canadian Application 971,606 filed September 28, 1966.

The non-aqueous or organic liquid can be any low viscosity compound or mixture substantially inert with respect to the powder and aqueous liquid, and should form the continuous phase. Suitable liquids include petroleum spirits e.g. Varsol (trademark), halogenated hydrocarbons, aromatic hydrocarbons, silicone fluids and light petroleum oils.

The aqueous liquid should preferentially wet the metal powder. It may be necessary or desirable to treat the particle surface to render it preferentially wetted by water e.g. by polar organic compounds substantially insoluble in the organic

liquid such as ethanolamine, wetting agents (e.g. soaps, detergents ...) and glycerine, or to add such polar compounds to the water phase. The aqueous liquid or non-gaseous fluid can be more viscous than the organic liquid -- and may comprise a dissolved or dispersed adhesive. The proportions of the aqueous liquid are not critical and optimum amounts vary for different material used. There should be sufficient to agglomerate the powder but insufficient to form large soft masses. Preferably about 5 to 75% by volume of the metal powder is used. The size of the final pellets is determined by the amount of aqueous liquid used and also by the factors mentioned in the following paragraph.

The container should be only partially filed e.g. to about 20 to 90% by vol. to allow a good translational motion of the agglomerates. The container geometry, shaking pattern and frequency, loading and the organic liquid viscosity should be selected to give the desired impact and ricocheting resonance. The container walls should be relatively inert to the organic and especially to the aqueous liquid. Tetrafluoroethylene polymers make a desirable wall surface.

By passing or recycling the organic liquid-plus-agglomerates through a series of rapidly rotating blades or vanes, sufficient impact and ricocheting action on the pellets may be achieved for some purposes. However, shaking in the container is preferred.

The metal powder is desirably lead or iron but other metals such as copper, aluminum, zinc etc. may be used. Where no adhesive is used the metal powder should be susceptible to cold welding. Lead, copper and alloys such as Wood's metal can be cold-welded under the impact. The particle size is not critical and can be the size used for pigments, powder metallurgy, fillers and other applications. A preferred powder size is about 0.1 - 100 micron diameter. The powder loading should be

less than about 35% by vol. of the organic liquid, or less than that giving an insufficiently fluid system.

The adhesive is not critical but should be chosen to give a suitable disintegration time and strength. The amount of the adhesive may range up to about 50 or more % by volume based on the metal powder. A preferred range is 10-20% vol. Adhesives in dispersed or dissolved form which have been used are polyvinyl acetate, commercial mucilage, polyvinyl alcohol, starch, white and orange shellac, sodium silicate, animal glue and dextrin (in order of decreasing disintegration times in water). Thermosetting or polymerizable adhesives dissolved or dispersed in water can also be used.

The following Examples are illustrative.

Example 1

The following ingredients were added to a polytetrafluoroethylene-lined cylindrical container (capacity 100 cc) having rounded ends and shaken in a three dimensional pattern in a Pica Blendor for 10 minutes.

Powdered lead (-200 mesh)	26 gm.
Petroleum aliphatic solvent (Varsol)	30 cc.
Polyvinyl acetate emulsion (55% solids)	1.6 cc.

Lead spheres about 0.080 inch diameter were obtained on separation from the solvent, and were dried at 100°C for 2 hours. The pellets contained about 25% adhesive by volume and had a crushing strength of more than 10 lbs. The density was about 9 gm/cc. (massive lead about 11.3). Disintegration time in water was about 10 days. Ballistic tests were satisfactory.

Example 2

Similar to Example 1 except the following proportions and a Spex Mixer Mill were used:

Lead powder (-325 mesh)	75 gm.
Petroleum aliphatic solvent (Varsol)	50 ml.

Example 2 continued

Polyvinyl acetate emulsion (48% solids in water)	3.0 ml.

Shaking for 10 minutes gave quite uniform spheres about 0.12 inch diameter and of density 8 gm/cc. Disintegration time in water varied from several days to two weeks.

Example 3

Similar to Example 1 except the following ingredients were used.

Iron powder (-325 mesh)	18 gm.
Petroleum aliphatic solvent (Varsol)	50 ml.
Commercial mucilage (45% solids in water)	1.9 ml.

Shaking for 10 min. gave quite uniform spheres about 0.06 inch diameter and of density 5 gm/cc.

The crushing strengths of the spheres from Examples 2 and 3 were approximately proportional to the square of the diameter indicating uniform binding throughout the pellet. Crushing strengths (calculated for one inch pellets) ranged from about 1200 - 2400 lbs and higher. The size of the pellets was varied slightly by changing the speed of shaking and/or the amount and composition of the adhesive.

Further examples with lead and adhesive showed that with less adhesive considerably increased density and a more permanent structure were obtained. In the absence of adhesive, bonds were produced apparently by a cold-welding or -forging effect. Densities as high as 10 were obtained indicating a void volume of about 10% only. Although these shot were very strong, accurate crushing strengths were difficult to estimate owing to plastic flow.

More permanent bonding of the primary particles (and more strength) is available through the selection of suitable

adhesives for each metal, the use of solvents (as bridging liquid) capable of allowing recrystallization of the adhesive solids at the junction points, the use of clean or activated particle surfaces and/or through a final sintering or heat treatment.

Claims

1. A process for forming strong pellets from finely divided metal powders in a non-aqueous liquid phase, the metals or alloys being cold-weldable when no adhesive is used comprising:

(a) adding the metal powder, and minor amounts of aqueous fluid to sufficient inert non-aqueous liquid to form the continuous phase in a fluid system.

(b) subjecting the fluid mixture to agitation to form dispersed agglomerates of powder and aqueous fluid in the non-aqueous liquid;

(c) causing the agglomerates to undergo a continued impact and ricocheting action against non-resilient surfaces at a glancing angle, and prolonging this action until the agglomerates are formed into the desired pellets; and

(d) removing the pellets from the non-aqueous liquid.

2. The process of claim 1 wherein the agglomerates are shaken in a three dimensional pattern in a closed partially-filled container.

3. The process of claim 2 wherein the container has rounded inner surfaces which are inert with respect to the two liquids.

4. The process of claims 1, 2 and 3 wherein the aqueous fluid consists essentially of water.

5. The process of claims 1, 2 and 3 wherein the aqueous fluid comprises an adhesive in amounts ranging up to about 50% vol. based on the metal.

6. The process of claims 1, 2 and 3 wherein the aqueous fluid comprises an adhesive which will disintegrate in a moist

environment.

7. The process of claims 1, 2 and 3 wherein the metal is lead of particle size -200 mesh and the pellet size is from about 0.01 to about 1 inch diameter.

8. The process of claims 1, 2 and 3 wherein the non-aqueous liquid is aliphatic hydrocarbon.

9. The process of claims 1, 2 and 3 including a further step of heat-treating the pellets.

10. Strong spherical agglomerates of powdered metal bonded by at least one of (a) a minor amount of an aqueous-base adhesive, and (b) cold-welding between powder particles.

11. Bird shot pellets according to claim 10 which will disintegrate in a moist environment, comprising agglomerated powdered lead bonded by a minor amount of a water-disintegratable adhesive.

12. Bird shot pellets according to claim 10 which will disintegrate in a moist environment, comprising agglomerated powdered iron bonded by a minor amount of a water-disintegratable adhesive.

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